The Kinetic Theory of a Special Type of Rigid Molecule.

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1. The present paper is an exercise in the classical kinetic theory, with no admixture of quantum theory, or of the modern theory of atomic structure. The researches of Chapman[*] and Enskog[†] suggest an attempt to see how far exact methods can be used when the molecule has rotational as well as translational energy. It is now well established that if λ is the thermal conductivity, μ the viscosity, and c_v the specific heat at constant volume of a monatomic gas, $\lambda/\mu c_v$ is nearly equal to 2·5. No exhaustive theory is yet in sight for polyatomic gases, but the views of Eucken[‡] are of great interest, and his formula $\lambda/\mu c_v = \frac{1}{4}(9\gamma - 5)$ agrees with many experiments. The present paper discusses the effect of energy of rotation on viscosity and thermal conductivity in a special case, and may help to elucidate certain points, notwithstanding the crudeness of the adopted model.

The need of a molecular model which shall lend itself to calculation has often been felt. In his first paper on the kinetic theory, Maxwell[§] considered the collision of perfectly elastic bodies of any form, and enunciated the theorem about energy of rotation which was afterwards included in the general doctrine of equipartition in the steady state. Of recent years more attention has been paid to slight departures from the steady state, with a view to obtaining a rigorous theory of thermal conductivity, diffusion, and viscosity. Jeans[||] considered the perfectly elastic collisions of smooth spheres whose centres of mass and figure are different. Approximations were made by neglecting powers of r/σ higher than the second, where r is the eccentricity and σ the diameter of the molecule, so that we have rather an unfortunate limiting case in which energy of rotation only adjusts itself infinitely slowly in comparison with that of translation; while the free path phenomena were not treated in detail. It appeared to the writer that there would be less trouble with the molecular model suggested by Bryan.[¶]

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[*] S. Chapman, 'Phil. Trans.,' A, vol. 216, p. 279 (1915); vol. 217, p. 115 (1916).

[†] D. Enskog, 'Inaug. Dissert.,' Upsala, 1917.

[‡] A. Eucken, 'Phys. Zeitschr.,' vol. 14, p. 324 (1913).

[§] J. C. Maxwell, 'Phil. Mag.' (4), vol. 20, p. 33 (1860); 'Collected Papers,' vol. 1, p. 406; see also L. Boltzmann, 'Sitzber. Preuss. Akad. Berlin,' p. 1395 (1888); 'Wiss. Abhandl.,' vol. 3, p. 366.

[||] J. H. Jeans, 'Phil. Trans.,' A, vol. 196, p. 399 (1901); 'Quart. J. Math.,' vol. 25, p. 224 (1904).

[¶] G. H. Bryan, 'Brit. Ass. Rep.,' p. 83 (1894).

Imagine two spheres to collide and grip each other, so as to bring the points of contact to relative rest. A small elastic deformation is produced, which we suppose to be released immediately afterwards, the force during release being equal to that at the corresponding stage of compression. Thus the relative velocity of the points of contact is reversed by collision.

Let O, O_1 be the centres of two identical molecules of mass M and radius a, P, P_1 the points of impact, $(-MI_x, -MI_y, -MI_z)$ the impulse at P on the first sphere and (MI_x, MI_y, MI_z) the impulse at P_1 on the second sphere. The direction-cosines of OO_1 are taken as (l, m, n). Let

u_x', u_y', u_z' be the linear velocity of the first sphere before collision,
$\omega_x', \omega_y', \omega_z'$ be the angular velocity of the first sphere before collision,
$u_{x1}', u_{y1}', u_{z1}'$ be the linear velocity of the second sphere before collision,
$\omega_{x1}', \omega_{y1}', \omega_{z1}'$ be the angular velocity of the second sphere before collision,
u_x, u_y, u_z be the linear velocity of the first sphere after collision,
$\omega_x, \omega_y, \omega_z$ be the angular velocity of the first sphere after collision,
u_{x1}, u_{y1}, u_{z1} be the linear velocity of the second sphere after collision,
$\omega_{x1}, \omega_{y1}, \omega_{z1}$ be the angular velocity of the second sphere after collision,

and write $\kappa = k^2/a^2$, where k is the radius of gyration of the sphere about any axis through the centroid. Then we have fifteen equations of the five types

$$\left.\begin{aligned} u_x' &= u_x + I_x, & \omega_x' &= \omega_x + \frac{mI_z - nI_y}{\kappa a} \\ u_{x1}' &= u_{x1} - I_x, & \omega_{x1}' &= \omega_{x1} + \frac{mI_z - nI_y}{\kappa a} \end{aligned}\right\}, \tag{1}$$

$$\begin{aligned} u_x' - ma\omega_z' + na\omega_y' - (u_{x1}' + ma\omega_{z1}' - na\omega_{y1}') \\ + u_x - ma\omega_z + na\omega_y - (u_{x1} + ma\omega_{z1} - na\omega_{y1}) = 0. \end{aligned} \tag{2}$$

Writing

$$\Theta_x = u_{x1} - u_x + ma(\omega_{z1} + \omega_z) - na(\omega_{y1} + \omega_y), \tag{3}$$

we find

$$\left.\begin{aligned} u_x' &= u_x + \frac{\kappa\Theta_x l + l(\Theta_x + m\Theta_y + n\Theta_z)}{1+\kappa}, & \omega_x' &= \omega_x + \frac{m\Theta_z - n\Theta_y}{a(1+\kappa)} \\ u_{x1}' &= u_{x1} - \frac{\kappa\Theta_x l + l(\Theta_x + m\Theta_y + n\Theta_z)}{1+\kappa}, & \omega_{x1}' &= \omega_{x1} + \frac{m\Theta_z - n\Theta_y}{a(1+\kappa)} \end{aligned}\right\}. \tag{4}$$

We note the following facts about this collision :—

(1) Accented and unaccented letters can be interchanged in equations (4), with definitions of Θ_x', Θ_y', Θ_z' of the same form as (3); thus equations (3) and (4) can be used also to calculate elements *after* collision from those *before* collision, for a given (l, m, n) physical possibility not being considered. It follows that the (twelfth order) Jacobian of transformation is numerically equal to 1.

(2) The formulæ are unchanged when the signs of l, m, n and the angular velocities are changed, leaving the linear velocities unaltered.

(3) The *rôle* of the two colliding molecules can be interchanged by changing the signs of l, m, n.

(4) There is no gain or loss of kinetic energy by the system.

2. Confining our attention to a single gas, the number of molecules in the volume element $dxdydz$ with velocities between u_x, u_y, u_z, and u_x+du_x, u_y+du_y, u_z+du_z, and angular velocities between ω_x, ω_y, ω_z, and $\omega_x+d\omega_x$, $\omega_y+d\omega_y$, $\omega_z+d\omega_x$, is written

$$f\,(t,\,x,\,y,\,z,\,u_x,\,u_y,\,u_z,\,\omega_x,\,\omega_y,\,\omega_z)\;dx\;dy\;dz\;du_x\;du_y\;du_z\;d\omega_x\;d\omega_y\;d\omega_z.$$

The external forces on a molecule are assumed to be statically equivalent to a force (MF_x, MF_y, MF_z), at the centre, where F is independent of the velocity.* Direct collision between molecules (u_x, u_y, u_z, ω_x, ω_y, ω_z) and (u_{x1}, u_{y1}, u_{z1}, ω_{x1}, ω_{y1}, ω_{z1}) is not possible with the direction-cosines l, m, n of equation (4), the direction-cosines $-l$, $-m$, $-n$ taking their place. The proof of the equation satisfied by f is well known.† The later proofs are free from a defect pointed out by Lorentz,‡ which would be quite fatal with a rigid molecule. Thus the direct collision just referred to does not give linear and angular velocities (u_x', u_y', u_z', ω_x', ω_y', ω_z') and (u_{x1}', u_{y1}', u_{z1}'; ω_{x1}', ω_{y1}', ω_{z1}') after collision; the nearest thing to an inverse collision is that molecules (u_x, u_y, u_z, $-\omega_x$, $-\omega_y$, $-\omega_z$) and (u_{x1}, u_{y1}, u_{z1}, $-\omega_{x1}$, $-\omega_{y1}$, $-\omega_{z1}$), colliding at ($-l$, $-m$, $-n$), give molecules (u_x', u_y', u_z', $-\omega_x'$, $-\omega_y'$, $-\omega_z'$) and (u_{x1}', u_{y1}', u_{z1}', $-\omega_{x1}'$ $-\omega_{y1}'$ $-\omega_{z1}'$) (see notes (1) and (2) of last article).

Writing $d\tau$ for the expression $du_xdu_ydu_zd\omega_xd\omega_yd\omega_z$ and $d\tau_1$ for $du_{x1}du_{y1}du_{z1}d\omega_{x1}d\omega_{y1}d\omega_{z1}$ we have

$$\int (f'f_1'-ff_1)\,\mathrm{V}\sigma^2\,d\mathrm{S}\,d\tau_1 = \frac{\partial f}{\partial t}+u_x\frac{\partial f}{\partial x}+u_y\frac{\partial f}{\partial y}+u_x\frac{\partial f}{\partial z}$$
$$+\mathrm{F}_x\frac{\partial f}{\partial u_x}+\mathrm{F}_y\frac{\partial f}{\partial u_y}+\mathrm{F}_z\frac{\partial f}{\partial u_z}, \qquad (5)$$

where

$$\mathrm{V} = l\,(u_{x1}-u_x)+m\,(u_{y1}-u_y)+n\,(u_{z1}-u_z). \qquad (6)$$

Here $\sigma = 2a$ is the diameter of the molecule and $d\mathrm{S}$ an element of solid angle in the direction (l, m, n), integration with respect to S being over that hemisphere which makes V positive.

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* For the general case see H. A. Lorentz, 'Abhandlungen über theoretische Physik,' vol. 1, p. 164 (1907).

† L. Boltzmann, 'Wien. Ber.,' vol. 66, Abth. 2, p. 324 (1872); vol. 72, p. 427 (1875); 'Wiss. Abhandl.,' vol. 1, p. 361; vol. 2, p. 1; 'Gastheorie,' vol. 1, p. 98.

‡ H. A. Lorentz, 'Wien. Ber.,' vol. 95, Abth. 2, p. 115 (1887); L. Boltzmann, *ibid.*, p. 153.

The advantages of Bryan's model will now be apparent. We have no angular positional co-ordinates in the equation, and no $\partial/\partial\omega$ terms on the right. From $\int(f'f_1'-ff_1)\,\mathrm{V}d\mathrm{S}d\tau_1 = 0$ in the equilibrium state we pass to $f'f_1' = ff_1$ for all possible collisions, notes (1) and (3) of Article 1 justifying the transformation of the integral

$$\int\phi\,(f'f_1'-ff_1)\,\mathrm{V}d\mathrm{S}d\tau d\tau_1 \text{ to } -\tfrac{1}{4}\int(\phi'+\phi_1'-\phi-\phi_1)(f'f_1'-ff_1)\,\mathrm{V}d\mathrm{S}d\tau d\tau_1.^*$$

Hence the distribution

$$\log f = \lambda\,\{u_x^2+u_y^2+u_z^2+\kappa a^2(\omega_x^2+\omega_y^2+\omega_z^2)\}+\mu u_x+\nu u_y+\rho u_z+\sigma \qquad (7)$$

is sufficient for equilibrium, though not proved to be necessary.

In a paper on the kinetic theory of a gas whose molecules are smooth rigid bodies of any form, Ishida[†] finds also linear terms in ω, but his reasoning seems to depend on an erroneous inclusion of the angular momentum of a molecule round its centroid in the class of summational invariants. The linear terms are said to be determined by the visible motion of rotation of the gas. With our present model, at least, there are weighty reasons against this; firstly, that excess angular velocity of one sign tends (unlike excess linear velocity) to disappear when two molecules collide; and, secondly, that for a gas rotating uniformly in a cylindrical vessel there is no need to assume a unilateral distribution of angular velocity. To prove the first point consider two groups of molecules with definite linear and angular velocities, which are within narrow limits of $(u_x, u_y, u_z, \omega_x, \omega_y, \omega_z)$ and $(u_{x1}, u_{y1}, u_{z1}, \omega_{x1}, \omega_{y1}, \omega_{z1})$ respectively. The number of collisions in which the line of centres is within an elementary solid angle $d\mathrm{S}$ near (l, m, n) is proportional to $\mathrm{V}d\mathrm{S}$, and we have to find the mean angular velocity after collision. Write

$$\alpha_x = \omega_{x1}+\omega_x, \ldots\ldots \quad \Phi_x = u_{x1}-u_x, \ldots\ldots$$

Then (3) and (4) give three equations of the type

$$\alpha_x' = \left\{1-\frac{2}{1+\kappa}(m^2+n^2)\right\}\alpha_x+\frac{2}{1+\kappa}(lm\alpha_y+nl\alpha_z) + \frac{2}{a(1+\kappa)}(m\Phi_z-n\Phi_y).$$

Take axes for the moment so that $\Phi_x = \Phi_y = 0$ and Φ_z is positive. Then

$$\alpha_x' = \left\{1-\frac{2}{1+\kappa}(m^2+n^2)\right\}\alpha_x+\frac{2}{1+\kappa}(lm\alpha_y+nl\alpha_z)+\frac{2m\Phi_z}{a(1+\kappa)},$$

$$\alpha_y' = \left\{1-\frac{2}{1+\kappa}(n^2+l^2)\right\}\alpha_y+\frac{2}{1+\kappa}(mn\alpha_z+lm\alpha_x)-\frac{2l\Phi_z}{a(1+\kappa)},$$

$$\alpha_z' = \left\{1-\frac{2}{1+\kappa}(l^2+m^2)\right\}\alpha_z+\frac{2}{1+\kappa}(nl\alpha_x+mn\alpha_y).$$

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[*] *Cf.* Boltzmann, 'Gastheorie,' vol. 1, pp. 119–121; Enskog, p. 24.

[†] Y. Ishida, 'Phys. Rev.,' vol. 10, p. 317 (1917).

We have $V = \Phi n_z$ and integration is over the hemisphere $n > 0$. The mean values of α_x', α_y', α_z' are given by

$$\pi\overline{\alpha_x'} = \int \alpha_x' n dS, \qquad \pi\overline{\alpha_y'} = \int \alpha_y' n dS, \qquad \pi\overline{\alpha_z'} = \int \alpha_z' n dS.$$

Terms after the first in the expressions for α_x', α_y', α_z' vanish on integration, so that

$$\pi\overline{\alpha_x'} = \alpha_x \int \left\{ n - \frac{2n}{1+\kappa}(m^2+n^2) \right\} dS, \quad \pi\overline{\alpha_y'} = \alpha_y \int \left\{ n - \frac{2n}{1+\kappa}(n^2+l^2) \right\} dS,$$

$$\pi\overline{\alpha_z'} = \alpha_z \int \left\{ n - \frac{2n}{1+\kappa}(l^2+m^2) \right\} dS.$$

Evaluating the integrals,

$$\overline{\alpha_x'} = \left\{ 1 - \frac{3}{2(1+\kappa)} \right\} \alpha_x, \qquad \overline{\alpha_y'} = \left\{ 1 - \frac{3}{2(1+\kappa)} \right\} \alpha_y,$$

$$\overline{\alpha_z'} = \left\{ 1 - \frac{1}{1+\kappa} \right\} \alpha_z.$$

Each of the three coefficients being numerically less than unity, the magnitude of the mean angular velocity after collision is less than $(\alpha_x^2 + \alpha_y^2 + \alpha_z^2)^{\frac{1}{2}}$.

As regards mass-rotation of the gas as a whole, the case of a monatomic gas rotating with uniform angular velocity is one of those for which Boltzmann* found an exact solution, and the proof applies also to the present molecular model. Boltzmann's solutions make both the left and right-hand sides of his equation (5) vanish. As far as the left-hand side is concerned, λ, μ, ν, ρ and σ in equation (7) may be any functions of x, y, z and t. The right-hand side vanishes if

$$\lambda, \sigma = \text{const.}, \quad \mu = y\Omega_z - z\Omega_y, \quad \nu = z\Omega_x - x\Omega_z, \quad \rho = x\Omega_y - y\Omega_x,$$

where Ω_x, Ω_y, Ω_z are constants, and the mass-motion is a uniform rotation with angular velocity $-\Omega/2\lambda$. Thus rotation of the gas as a whole does not necessarily imply preponderant rotation of the separate molecules about any axis.

3. The general idea underlying all recent theories of viscosity and thermal conduction in gases is that of successive approximation, initiated by Maxwell† and applied to Boltzmann's equation by Brillouin,‡ Lorentz,§ and

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* L. Boltzmann, 'Wien. Ber.,' vol. 74, Abth. 2, p. 539 (1876); 'Wiss. Abhandl.,' vol. 2, p. 90; 'Gastheorie,' vol. 1, p. 139.

† J. C. Maxwell, 'Phil. Trans.,' vol. 157, p. 80 (1866); 'Collected Papers,' vol. 2, p. 68.

‡ M. Brillouin, 'Ann. Chim. Phys.,' (7), vol. 20, p. 451 (1900).

§ H. A. Lorentz, 'Archives Néerland.,' vol. 10, p. 343 (1905); 'Theory of Electrons,' 2nd ed., p. 267.

Hilbert* Hilbert's argument is essentially as follows. Writing D for the operator

$$\frac{\partial}{\partial t}+u_x\frac{\partial}{\partial x}+u_y\frac{\partial}{\partial y}+u_z\frac{\partial}{\partial z}+\mathrm{F}_x\frac{\partial}{\partial u_x}+\mathrm{F}_y\frac{\partial}{\partial u_y}+\mathrm{F}_z\frac{\partial}{\partial u_z}, \tag{8}$$

equation (5) becomes

$$\int (f'f_1'-ff_1)\,\mathrm{V}d\mathrm{S}\,d\tau_1 = \frac{1}{\sigma^2}\,\mathrm{D}f.$$

Expanding f in the form

$$f = \Phi+\frac{\Psi}{\sigma^2}+\frac{\mathrm{X}}{\sigma^4}+\ \dots,$$

and equating coefficients of the various powers of $1/\sigma^2$, we have a set of equations to determine Φ, Ψ, ..., of which the first two are

$$\int (\Phi'\Phi_1'-\Phi\Phi_1)\,\mathrm{V}\,d\mathrm{S}\,d\tau_1 = 0, \tag{9}$$

$$\int (\Phi_1'\Psi'+\Phi'\Psi_1'-\Phi_1\Psi-\Phi\Psi_1)\,\mathrm{V}\,d\mathrm{S}\,d\tau_1 = \mathrm{D}\Phi. \tag{10}$$

For the solution of (9) we take

$$\Phi = \frac{\rho\mathrm{M}^2a^3\kappa^{3/2}}{8\pi^3\mathrm{R}^3\mathrm{T}^3}\exp\left[-\frac{\mathrm{M}}{2\mathrm{RT}}\left\{(u_x-v_x)^2+(u_y-v_y)^2+(u_z-v_z)^2+\kappa a^2(\omega_x^2+\omega_y^2+\omega_z^2)\right\}\right], \tag{11}$$

where ρ is the density, T the absolute temperature and (v_x, v_y, v_z) the mean velocity of the gas at (x, y, z) at time t, and R the universal gas constant $1{\cdot}35\times10^{-16}$. This choice of parameters makes $\int f\psi\,d\tau = \int \Phi\psi\,d\tau$ for any of the five functions

$$\psi = 1,\quad u_x,\quad u_y,\quad u_z,\quad u_x^2+u_y^2+u_z^2+\kappa a^2(\omega_x^2+\omega_y^2+\omega_z^2).$$

Following Brillouin and Hilbert we write $\Psi = \Phi\phi$, so that we have to the first order in $1/\sigma^2$

$$f = \Phi\,(1+\phi/\sigma^2), \tag{12}$$

where ϕ is given by the equation

$$\int \Phi_1\,(\phi'+\phi_1'-\phi-\phi_1)\,\mathrm{V}\,d\mathrm{S}\,d\tau_1 = \mathrm{D}\,(\log\Phi), \tag{13}$$

and satisfies the additional conditions

$$\int \Phi\phi\,d\tau = \int \Phi\phi u_x d\tau = \int \Phi\phi u_y\,d\tau = \int \Phi\phi u_z d\tau$$
$$= \int \Phi\phi\,\{u_x^2+u_y^2+u_z^2+\kappa a^2(\omega_x^2+\omega_y^2+\omega_z^2)\}\,d\tau = 0. \tag{14}$$

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* D. Hilbert, 'Math. Ann.,' vol. 72, p. 565 (1912); 'Lineare Integralgleichungen,' p. 270.

4. Following Hilbert and Enskog, it is convenient to introduce the new variables

$$\left.\begin{aligned} p_x &= \left(\frac{\mathrm{M}}{2\,\mathrm{RT}}\right)^{\frac{1}{2}}(u_x-v_x), & p_y &= \left(\frac{\mathrm{M}}{2\,\mathrm{RT}}\right)^{\frac{1}{2}}(u_y-v_y), & p_z &= \left(\frac{\mathrm{M}}{2\,\mathrm{RT}}\right)^{\frac{1}{2}}(u_z-v_z) \\ q_x &= \left(\frac{\mathrm{M}\kappa}{2\,\mathrm{RT}}\right)^{\frac{1}{2}}a\omega_x, & q_y &= \left(\frac{\mathrm{M}\kappa}{2\,\mathrm{RT}}\right)^{\frac{1}{2}}a\omega_y, & q_z &= \left(\frac{\mathrm{M}\kappa}{2\,\mathrm{RT}}\right)^{\frac{1}{2}}a\omega_z \end{aligned}\right\}, \tag{15}$$

and write

$$p^2 = p_x^2+p_y^2+p_z^2, \quad q^2 = q_x^2+q_y^2+q_z^2, \quad dr = dp_x\,dp_y\,dp_z\,dq_x\,dq_y\,dq_z, \tag{16}$$

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t}+v_x\frac{\partial}{\partial x}+v_y\frac{\partial}{\partial y}+v_z\frac{\partial}{\partial z}. \tag{17}$$

Then if no external forces are acting, equation (13) becomes

$$\begin{aligned} &\int \exp(-p_1^2-q_1^2)(\phi'+\phi_1'-\phi-\phi_1)\,\mathrm{V}\,d\mathrm{S}\,dr_1 \\ &\quad = \frac{\mathrm{M}\pi^3}{\rho}\Bigg[\left(\frac{\mathrm{M}}{2\,\mathrm{RT}}\right)^{\frac{1}{2}}\frac{d}{dt}\log\left(\frac{\rho}{\mathrm{T}^3}\right)+\left(\frac{\mathrm{M}}{2\,\mathrm{RT}}\right)^{\frac{1}{2}}\frac{p^2+q^2}{\mathrm{T}}\frac{d\mathrm{T}}{dt} \\ &\qquad\qquad +\frac{\mathrm{M}}{\mathrm{RT}}\left(p_x\frac{dv_x}{dt}+p_y\frac{dv_y}{dt}+p_z\frac{dv_z}{dt}\right) \\ &\qquad +\left(p_x\frac{\partial}{\partial x}+p_y\frac{\partial}{\partial y}+p_z\frac{\partial}{\partial z}\right)\log\left(\frac{\rho}{\mathrm{T}^3}\right)+\frac{p^2+q^2}{\mathrm{T}}\left(p_x\frac{\partial\mathrm{T}}{\partial x}+p_y\frac{\partial\mathrm{T}}{\partial y}+p_z\frac{\partial\mathrm{T}}{\partial z}\right) \\ &\qquad +2\left(\frac{\mathrm{M}}{2\,\mathrm{RT}}\right)^{\frac{1}{2}}\left\{p_x^2\frac{\partial v_x}{\partial x}+\ldots+\ldots+p_yp_z\left(\frac{\partial v_z}{\partial y}+\frac{\partial v_y}{\partial z}\right)+\ldots+\ldots\right\}\Bigg], \end{aligned} \tag{18}$$

where we write with a slight change of notation

$$\mathrm{V} = l(p_{x1}-p_x)+m(p_{y1}-p_y)+n(p_{z1}-p_z). \tag{19}$$

With a similar slight change in equations (3) and (4) we have

$$\left.\begin{aligned} p_x' &= p_x+\frac{\kappa\Theta_x+l\mathrm{V}}{1+\kappa}, & q_x' &= q_x+\frac{\kappa^{\frac{1}{2}}(m\Theta_z-n\Theta_y)}{1+\kappa} \\ p_{x1}' &= p_{x1}-\frac{\kappa\Theta_x+l\mathrm{V}}{1+\kappa}, & q_{x1}' &= q_{x1}+\frac{\kappa^{\frac{1}{2}}(m\Theta_z-n\Theta_y)}{1+\kappa} \end{aligned}\right\} \tag{20}$$

where
$$\Theta_x = p_{x1}-p_x+\kappa^{-\frac{1}{2}}m(q_{z1}+q_z)-\kappa^{-\frac{1}{2}}n(q_{y1}+q_y). \tag{21}$$

In order that equations (18) may be soluble, certain conditions must be satisfied, which, as Hilbert pointed out, are the approximate hydrodynamical equations, together with the equations of continuity and energy. Writing Q for the right-hand side of equation (18), we have

$$\begin{aligned} &\int \exp(-p^2-q^2)\,\mathrm{Q}\psi\,dr \\ &\qquad = \int \exp(-p^2-q^2-p_1^2-q_1^2)(\phi'+\phi_1'-\phi-\phi_1)\,\psi\mathrm{V}\,d\mathrm{S}\,dr\,dr_1, \end{aligned}$$

where ψ is an arbitrary function of p_x, p_y, p_z, q_x, q_y, q_z, subject to certain conditions of integrability. Writing $[\phi, \psi]$, in Enskog's notation, for the integral on the right, we find as before

$$[\phi, \psi] = -\tfrac{1}{4}\int \exp\left(-p^2-q^2-p_1^2-q_1^2\right) \\ (\phi'+\phi_1'-\phi-\phi_1)(\psi'+\psi_1'-\psi-\psi_1)\,\mathrm{V}\,d\mathrm{S}\,dr\,dr_1,$$

showing that $[\phi, \psi] = [\psi, \phi]$. It follows that necessary conditions for the solubility of (18) are $\int \exp(-p^2-q^2)\,\mathrm{Q}\psi\,dr = 0$, where ψ is any of the functions $1, p_x, p_y, p_z, p^2+q^2$. The right-hand side of (18) is of the form

$$\mathrm{Q} = \mathrm{Q}_{00}+\mathrm{Q}_0(p^2+q^2)+\{\mathrm{Q}_{x0}+\mathrm{Q}_x(p^2+q^2)\}p_x+\ldots \\ +\mathrm{Q}_{xx}p_x^2+\ldots+\mathrm{Q}_{yz}p_yp_z+\ldots,$$

where the coefficients $\mathrm{Q}_{00}, \ldots\ldots$ are independent of $p_x, p_y, p_z, q_x, q_y, q_z$. Evaluating the integrals we find

$$\mathrm{Q}_{00} = 0, \qquad \mathrm{Q}_0 = -\tfrac{1}{6}(\mathrm{Q}_{xx}+\mathrm{Q}_{yy}+\mathrm{Q}_{zz}), \qquad \mathrm{Q}_{x0} = -4\mathrm{Q}_x, \\ \mathrm{Q}_{y0} = -4\mathrm{Q}_y, \qquad \mathrm{Q}_{z0} = -4\mathrm{Q}_z.$$

Using these equations to remove the d/dt terms from (18), it becomes

$$\int \exp(-p_1^2-q_1^2)(\phi'+\phi_1'-\phi-\phi_1)\,\mathrm{V}\,d\mathrm{S}\,dr_1 \\ = \mathrm{Q}_x(p^2+q^2-4)p_x+\ldots+\mathrm{Q}_{xx}\{p_x^2-\tfrac{1}{6}(p^2+q^2)\} \\ +\ldots+\mathrm{Q}_{yz}p_yp_z+\ldots, \tag{22}$$

where

$$\mathrm{Q}_x = \frac{\mathrm{M}\pi^3}{\rho}\frac{1}{\mathrm{T}}\frac{\partial \mathrm{T}}{\partial x}, \qquad \mathrm{Q}_{xx} = \frac{2\mathrm{M}\pi^3}{\rho}\left(\frac{\mathrm{M}}{2\mathrm{RT}}\right)^{\frac{1}{2}}\frac{\partial v_x}{\partial x}, \\ \mathrm{Q}_{yz} = \frac{2\mathrm{M}\pi^3}{\rho}\left(\frac{\mathrm{M}}{2\mathrm{RT}}\right)^{\frac{1}{2}}\left(\frac{\partial v_z}{\partial y}+\frac{\partial v_y}{\partial z}\right). \tag{23}$$

It remains to limit the form of ϕ.* We must have by consideration of orthogonal invariance, with due regard to (14),

$$\phi = \mathrm{Q}_x\phi_x+\mathrm{Q}_y\phi_y+\mathrm{Q}_z\phi_z+\mathrm{Q}_{xx}\phi_{xx}+\ldots+\mathrm{Q}_{yz}\phi_{yz}+\ldots, \tag{24}$$

where

$$\left.\begin{aligned} \phi_x &= \mathrm{P}_0p_x+\mathrm{P}_1q_x \\ \phi_{xx} &= \mathrm{P}_2(p_x^2-\tfrac{1}{3}p^2)+\mathrm{P}_3\{p_xq_x-\tfrac{1}{3}(p_xq_x+p_yq_y+p_zq_z)\}+\mathrm{P}_4(q_x^2-\tfrac{1}{3}q^2) \\ \phi_{yz} &= \mathrm{P}_2p_yp_z+\mathrm{P}_3(p_yq_z+p_zq_y)+\mathrm{P}_4q_yq_z \end{aligned}\right\}, \tag{25}$$

and $\mathrm{P}_0, \ldots \mathrm{P}_4$ are functions of $p^2, q^2, p_xq_x+p_yq_y+p_zq_z$ only. Writing

$$\mathrm{I}(\phi) \equiv \int \exp(-p_1^2-q_1^2)(\phi'+\phi_1'-\phi-\phi_1)\,\mathrm{V}\,d\mathrm{S}\,dr_1, \tag{26}$$

the functions $\mathrm{P}_0, \ldots$ have to be found from the equations

$$\left.\begin{aligned} \mathrm{I}(\phi_x) &= (p^2+q^2-4)p_x \\ \mathrm{I}(\phi_{xx}) &= p_x^2-\tfrac{1}{6}(p^2+q^2) \end{aligned}\right\}. \tag{27}$$

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* *Cf.* Brillouin, *loc. cit.*; H. A. Lorentz, 'Vorträge über die kinetische Theorie der Materie,' p. 185 (1914).

Equations (14) may be written

$$\left.\begin{aligned} \int \exp(-p^2-q^2)\,\phi\psi\,dr &= 0 \\ \text{where} \qquad \psi &= 1,\ p_x,\ p_y,\ p_z,\ p^2+q^2 \end{aligned}\right\}. \tag{28}$$

5. Following Enskog, we attempt a series solution of (27). The functions are made to satisfy (28), and are of the following types :—

Conductivity type.

$$(1)\ \phi = \left[p^{2r} q^{2s} (p_x q_x + p_y q_y + p_z q_z)^{2t} - \frac{8\Gamma(r+t+\frac{5}{2})\,\Gamma(s+t+\frac{3}{2})}{3\pi(2t+1)}\right] p_x,$$

$$(2)\ \phi = p^{2r} q^{2s} (p_x q_x + p_y q_y + p_z q_z)^{2t+1} p_x,$$

$$(3)\ \phi = p^{2r} q^{2s} (p_x q_x + p_y q_y + p_z q_z)^{2t} q_x,$$

$$(4)\ \phi = \left[p^{2r} q^{2s} (p_x q_x + p_y q_y + p_z q_z)^{2t+1} - \frac{16\Gamma(r+t+\frac{5}{2})\,\Gamma(s+t+\frac{5}{2})}{3\pi(2t+3)} (p_x q_x + p_y q_y + p_z q_z)\right] q_x.$$

Viscosity type.

$$(1)\ \phi = p^{2r} q^{2s} (p_x q_x + p_y q_y + p_z q_z)^{t} (p_x{}^2 - \tfrac{1}{3}p^2),$$

$$(2)\ \phi = p^{2r} q^{2s} (p_x q_x + p_y q_y + p_z q_z)^{t} (q_x{}^2 - \tfrac{1}{3}q^2),$$

$$(3)\ \phi = p^{2r} q^{2s} (p_x q_x + p_y q_y + p_z q_z)^{t} \{p_x q_x - \tfrac{1}{3}(p_x q_x + p_y q_y + p_z q_z)\}.$$

To solve the first of equations (27) write

$$\phi_x = \Sigma c_n \phi_n, \tag{29}$$

where c_1, c_2, ... are constant coefficients and ϕ_1, ϕ_2, ... functions of the conductivity type. Write also

$$\left.\begin{aligned} \alpha_n &= \int \exp(-p^2-q^2)(p^2+q^2-4)\,p_x \phi_n\,dr \\ a_{mn} = a_{nm} = [\phi_m, \phi_n] &= \int \exp(-p^2-q^2)\,\mathrm{I}(\phi_m)\,\phi_n\,dr \end{aligned}\right\}. \tag{30}$$

Then the quantities α_n, a_{mn} are known by quadrature, and (27) gives

$$\left.\begin{aligned} c_1 a_{11} + c_2 a_{12} + \dots &= \alpha_1 \\ c_1 a_{21} + c_2 a_{22} + \dots &= \alpha_2 \\ \dots\dots\dots\dots& \end{aligned}\right\}. \tag{31}$$

These are the equations for the assumed coefficients. Chapman and Enskog have shown that terms of the first three degrees account for about 98 per cent. of the thermal conductivity and viscosity of a monatomic gas. It will be convenient, though not theoretically necessary, to neglect terms of degree higher than the third, thus obtaining a theory of the same approximation as Chapman's first theory.* We take

$$\left.\begin{aligned} \phi_1 &= (p^2-\tfrac{5}{2})p_x, & \phi_2 &= (q^2-\tfrac{3}{2})p_x, & \phi_3 &= (p_x q_x + p_y q_y + p_z q_z)\,p_x \\ \phi_4 &= q_x, & \phi_5 &= p^2 q_x, & \phi_6 &= q^2 q_x \end{aligned}\right\}. \tag{32}$$

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* S. Chapman, 'Phil. Trans.,' A, vol. 211, p. 433 (1911).

Evaluation of the integrals (30) is simplified by observing that only even powers of $\kappa^{\frac{1}{2}}$ occur in $\mathrm{I}(\phi_n)$, since the change from $\kappa^{\frac{1}{2}}$ to $\kappa^{-\frac{1}{2}}$ merely interchanges the *rôle* of two colliding molecules. The work is not laborious, but would become so if carried to a higher degree than the third. We find

$$\left.\begin{gathered}\alpha_1 = \tfrac{5}{4}\pi^3, \qquad \alpha_2 = \tfrac{3}{4}\pi^3, \qquad \alpha_3 = \alpha_4 = \alpha_5 = \alpha_6 = 0, \\ a_{11} = -\frac{(17\kappa+4)(2\pi)^{\frac{1}{2}}\pi^6}{3(1+\kappa)^2}, \quad a_{12} = \frac{5\kappa(2\pi)^{\frac{1}{2}}\pi^6}{3(1+\kappa)^2}, \quad a_{13} = a_{14} = a_{15} = a_{16} = 0, \\ a_{21} = \frac{5\kappa(2\pi)^{\frac{1}{2}}\pi^6}{3(1+\kappa)^2}, \qquad a_{22} = -\frac{(2\kappa^2+2\kappa+1)(2\pi)^{\frac{1}{2}}\pi^6}{(1+\kappa)^2}, \\ a_{23} = a_{24} = a_{25} = a_{26} = 0, \end{gathered}\right\}. \tag{33}$$

It follows that $c_3 = c_4 = c_5 = c_6 = 0$, and c_1, c_2 are given by the equations

$$c_1 a_{11} + c_2 a_{12} = \alpha_1, \qquad c_1 a_{21} + c_2 a_{22} = \alpha_2.$$

Hence

$$\begin{aligned} c_1 &= -\frac{30\kappa^2+45\kappa+15}{102\kappa^3+101\kappa^2+75\kappa+12}\,\frac{3(1+\kappa)^2}{4\pi^3(2\pi)^{\frac{1}{2}}}, \\ c_2 &= -\frac{76\kappa+12}{102\kappa^3+101\kappa^2+75\kappa+12}\,\frac{3(1+\kappa)^2}{4\pi^3(2\pi)^{\frac{1}{2}}}. \end{aligned} \tag{34}$$

To deal with viscosity we write $\phi_{xx} = c_7\phi_7 + c_8\phi_8 + c_9\phi_9$, where

$$\phi_7 = p_x{}^2 - \tfrac{1}{3}p^2, \quad \phi_8 = q_x{}^2 - \tfrac{1}{3}q^2, \quad \phi_9 = p_x q_x - \tfrac{1}{3}(p_x q_x + p_y q_y + p_z q_z) \tag{35}$$

and

$$\alpha_n = \int \exp(-p^2-q^2)\{p_x{}^2 - \tfrac{1}{6}(p^2+q^2)\}\,\phi_n\,dr, \tag{36}$$

a_{mn} remaining as in (30). We find

$$\left.\begin{gathered}\alpha_7 = \tfrac{1}{3}\pi^3, \qquad \alpha_8 = \alpha_9 = 0, \\ a_{77} = -\frac{4(13\kappa+6)(2\pi)^{\frac{1}{2}}\pi^6}{45(1+\kappa)^2}, \qquad a_{78} = a_{79} = 0 \end{gathered}\right\}. \tag{37}$$

Thus to our present order of approximation $\phi_{xx} = c_7\phi_7$, where

$$c_7 = -\frac{15(1+\kappa)^2}{4(13\kappa+6)\,\pi^3(2\pi)^{\frac{1}{2}}}. \tag{38}$$

6. Considering only the Q_x term in (24), the heat flow per cm.^{2} (in mechanical units) is

$$\tfrac{1}{2}\mathrm{M}\int f(u_x-v_x)\{(u_x-v_x)^2+(u_y-v_y)^2+(u_z-v_z)^2+\kappa a^2(\omega_x{}^2+\omega_y{}^2+\omega_z{}^2)\}\,d\tau,$$

where

$$f = \Phi + \frac{\mathrm{M}^3 a^3 \kappa^{3/2}}{8\mathrm{R}^3\mathrm{T}^4\sigma^2}\frac{\partial \mathrm{T}}{\partial x}\exp(-p^2-q^2)(c_1\phi_1+c_2\phi_2),$$

from (12) and (29). The first term in f contributes nothing to the flow.

Replacing $\partial T/\partial x$ by -1, we have an expression for the thermal conductivity, which becomes on reduction

$$\lambda = -\frac{\pi^3}{4\sigma^2}\left(\frac{2R^3T}{M}\right)^{\frac{1}{2}}(5c_1+3c_2),$$

or

$$\lambda = \frac{9}{16\sigma^2}\left(\frac{R^3T}{\pi M}\right)^{\frac{1}{2}}\frac{(1+\kappa)^2(50\kappa^2+151\kappa+37)}{102\kappa^3+101\kappa^2+75\kappa+12}. \tag{39}$$

The case in which $\kappa \to \infty$ is of no physical importance, but it is curious to see why $\lambda \to \infty$ in this case. Rotational motion is practically absent, and the effect of a collision from (4) is to transfer each velocity to the other molecule, virtually as if there had been no collision at all. The conductivity has a finite limit as $\kappa \to 0$, notwithstanding that $\omega \to \infty$ in the steady state.

Considering only the viscosity terms in (24), the X_x component of stress in the gas is given by

$$\begin{aligned} X_x - p &= M\int f\left[(u_x-v_x)^2-\tfrac{1}{3}\left\{(u_x-v_x)^2+(u_y-v_y)^2+(u_z-v_z)^2\right\}\right]d\tau \\ &= \frac{M\pi^3}{3\sigma^2}\left(\frac{2RT}{M}\right)^{\frac{1}{2}}c_7\left(2\frac{\partial v_x}{\partial x}-\frac{\partial v_y}{\partial y}-\frac{\partial v_z}{\partial z}\right) \end{aligned}$$

on reduction. Identifying the coefficient of $2\dfrac{\partial v_x}{\partial x}-\dfrac{\partial v_y}{\partial y}-\dfrac{\partial v_z}{\partial z}$ with $-\frac{2}{3}\mu$ and substituting from (38) we have

$$\mu = \frac{15}{8\sigma^2}\left(\frac{MRT}{\pi}\right)^{\frac{1}{2}}\frac{(1+\kappa)^2}{13\kappa+6}. \tag{40}$$

Also $c_v = 3R/M$, so that

$$\frac{\lambda}{\mu c_v} = \frac{(13\kappa+6)(50\kappa^2+151\kappa+37)}{10(102\kappa^3+101\kappa^2+75\kappa+12)}. \tag{41}$$

For $\kappa = 0, \frac{2}{5}$, and 1 we have $\lambda/\mu c_v = 1{\cdot}85, 1{\cdot}82, 1{\cdot}56$ respectively. Eucken's value corresponding to $\gamma = \frac{4}{3}$ is $\lambda/\mu c_v = 1{\cdot}75$; experiment gives $\gamma = 1{\cdot}33$ and $\lambda/\mu c_v = 1{\cdot}80$ for chlorine. It is not intended to suggest that the evidence supports any particular model; only that Eucken's number is as well confirmed as we can expect, seeing that $\lambda/\mu c_v$ does not depend on γ alone. Qualitative writers have often conjectured that viscosity is but little affected by rotation of the molecule. With our model, μ changes in the ratio 1 : 1·26 as κ changes from 0 to 1, and the lower value is the same as that of a monatomic gas in Chapman's first approximation. Another much debated matter is the partition of transported energy between the translational and rotational kinds in thermal conduction. As far as our theory goes, we find

$$\frac{\text{transported rotational energy}}{\text{transported translational energy}} = \frac{4(19\kappa+3)}{25(2\kappa^2+3\kappa+1)}, \tag{42}$$

which changes from 0·48 to 0·59 as κ changes from 0 to 1, with a maximum of 0·67 in between. It is difficult to imagine a model more effective in converting linear into angular velocity, and *vice versâ*, so that 70 per cent. may well be an upper limit of the relative efficiency of transport of rotational and translational energy.

The Specific Heats of Air, Steam and Carbon Dioxide.

By Sir R. T. Glazebrook, F.R.S.

(Received March 6, 1922.)

In a recent number* is a paper by Mr. W. D. Womersley bearing the above title, in which an account is given of a determination of specific heats of the gases named, employing a calorimeter designed by the late Prof. B. Hopkinson.

Mr. Womersley's experiments extended over the range 1000° C. to 2000°, and he states that the lower parts have been filled in from the researches of Swann and Holborn and Henning.

The results are given in a Table on p. 486 for every 100° C. up to 2000°. Swann's experiments were made at temperatures of 20° C. and 100° C., so that the range of values from 200° to 1000° depends on the work of Holborn and Henning, and, unfortunately, some error has been made in connection with their results.

They expressed these as the mean specific heat at constant pressure between 0° C. and the temperature of the observation—in the case of steam between 100° C. and the observation temperature.

Mr. Womersley has transformed their figures into mean volumetric heat per gramme-molecule, but I have been unable to deduce his figures from those given by Holborn and Henning, and, in view of the importance of the matter, it seems desirable to call attention to the discrepancy.

Holborn and Henning, in their paper,† give—Table VIII—their experimental results, and also the results obtained from a formula which expresses the experimental results within, in most cases less than 1 per cent. In the case of steam, two formulæ, which differ but slightly, are given, while in Table IX (p. 842) are stated the results at every 200° C. up to 1400° C.

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* 'Roy. Soc. Proc.,' A, vol. 100, p. 483.

† 'Annalen des Physik,' vol. 23, p. 809 (1907).